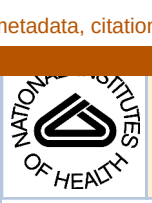

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Dense Nonaqueous Phase Liquids at Former Manufactured Gas Plants: Challenges to Modeling and Remediation

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Abstract

The remediation of dense non-aqueous phase liquids (DNAPLs) in porous media continues to be one of the most challenging problems facing environmental scientists and engineers. Of all the environmentally relevant DNAPLs, tars in the subsurface at former manufactured gas plants (FMGP's) pose one of the biggest challenges due to their complex chemical composition and tendency to alter wettability. To further our understanding of these complex materials, we consulted historic documentation to evaluate the impact of gas manufacturing on the composition and physicochemical nature of the resulting tars. In the recent literature, most work to date has been focused in a relatively narrow portion of the expected range of tar materials, which has yielded a bias toward samples of relatively low viscosity and density. In this work, we consider the dissolution and movement of tars in the subsurface, models used to predict these phenomena, and approaches used for remediation. We also explore the open issues and detail important gaps in our fundamental understanding of these extraordinarily complex systems that must be resolved to reach a mature level of understanding.

Keywords

Manufactured gas; Coal tar; Water-gas tar; Oil-gas tar; Polycyclic aromatic hydrocarbons; Groundwater; Dissolution; Mass transfer; Remediation; Natural attenuation

1 Introduction

Prior to the widespread use of natural gas, cities and towns throughout the U.S. and Europe relied upon gas manufactured from coal and oil. In the U.S. alone, several thousand manufactured gas plants existed between the early 1800's to the 1950's (U.S. EPA, 1993). During this time, there were numerous documented examples of groundwater contamination, though its persistence and the potential for further migration was not well understood (Harkins et al., 1988). In the present day, many of these sites are located in the heart of urban areas and are attractive sites for redevelopment. Wastes at FMGP's have led to contaminated soils, groundwater, and sediments, which can hinder redevelopment efforts and may pose a risk to human health and the environment.

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One of the primary waste streams from gas production is tar, an opaque viscous liquid that is enriched in high molecular weight compounds. Large volumes of tar were often disposed of in pits or landfilled on-site, after mixing with subsurface materials (Murphy et al., 2005). Over the many decades since these wastes were generated, tar can migrate from these primary source zones (Harkins et al., 1988). Because tars are DNAPLs, they tend to migrate downward and have the potential to act as long-term sources of dissolved phase contaminants. The specific contaminants of concern in tars can vary depending on the gas manufacturing process; however, all tars contain polycyclic aromatic hydrocarbons (PAH's) (Harkins et al., 1988). PAH's are a class of compounds containing several known carcinogens (U.S. EPA, 1993).

Despite the large number of sites and documented cases of groundwater contamination, tars are not as widely studied when compared to other environmentally relevant DNAPLs such as chlorinated solvents. One obvious limitation is access to tar DNAPLs. Whereas chlorinated solvents can be purchased commercially, samples of tar are obtained from former disposal pits or retrieved from groundwater wells. Tars are also difficult to work with in a laboratory setting. They can be highly viscous and contain hundreds of compounds making them physically and analytically challenging.

The physicochemical properties of tars are also very different from single component DNAPLs such as tetrachloroethylene (PCE) and trichloroethene (TCE). The movement and dissolution of these chlorinated solvents is governed largely by their high values of interfacial tension (IFT) and intermediate solubilities. In contrast, tars have a relatively low IFT, but they are prone to alter system wettability (Barranco and Dawson, 1999). Thus, remediation technologies that have been successful for PCE and TCE contaminated media, may not be applicable to tar contaminated media.

Though much of the recent literature refers to tars from FMGP's as "coal tar," historical documents make distinctions between tars to reflect the underlying manufacturing process (e.g., coal tar, water-gas tar, and oil-gas tar) (Rhodes, 1966a;b). These distinctions are important to understand because the manufacturing process can have a significant impact on tar composition (Rhodes, 1966a;b; Harkins et al., 1988; Murphy et al., 2005; Hamper, 2006). As an example, one of the most studied tars is from a FMGP in Stroudsburg, PA. This was the first site in the U.S. to receive emergency funding through the U.S. Environmental Protection Agency's Superfund Program (Villaume, 1984). In the literature, tars from this site are referred to as coal tars. In fact, the Stroudsburg FMGP used a process resulting in what is historically referred to as water-gas tars, explaining their low density and viscosity (Harkins et al., 1988).

The overall objective of this work is to identify gaps in our fundamental understanding of tar DNAPLs, limiting our ability to predict tar behavior and to design more effective in-situ remediation approaches. We believe these wastes pose a more difficult remediation challenge when compared to contaminated soils, which, in many cases, can be excavated for ex-situ treatment. Slow moving tar DNAPL plumes can also be the underlying source of sediment contamination. Specific objectives of this work are: (1) to review data on tar chemical composition, (2) to evaluate how composition affects tar behavior, (3) to critique modeling efforts for predicting the impact of tar in the subsurface, and (4) to outline the most pressing open issues. The focus of this work is the peer-reviewed scientific literature, rather than the gray literature, consisting of site-specific technical reports and industry documents. We also specifically focus on the U.S. manufactured gas industry, though major differences between the U.S. and European industries are noted along with differences in tar composition.

2 Sources

Manufactured gas plants were used extensively in the early part of the 20th century to produce gas from coal or oil. In 1812, the first commercial gas works was established in London to

provide street lighting (Rhodes, 1945). The establishment of gas works throughout cities in Europe and the U.S. soon followed. In the U.S., the first commercial gas works was established in Baltimore in 1816 (Castaneda, 1999). By the 1900's, electricity filled most lighting needs while manufactured gas became widely used for home heating and cooking. After World War II, the market for manufactured gas began to decline with the increasing availability of natural gas. By the 1960's, extensive natural gas pipelines were constructed in the U.S.; consequently, manufactured gas became obsolete (Castaneda, 1999). Across Europe, similar pressures from natural gas and competing petroleum products led to a significant decline in manufactured gas use after the late 1950's (Rhodes, 1945).

The three predominant types of gases manufactured for distribution included: coal gas, carburetted water gas, and oil gas (Harkins et al., 1988). Coal gas is a by-product of carbonization, also referred to as gasification. In this process, bituminous coal is heated in a sealed chamber and the volatiles are collected (Porter, 1924). The coal is also converted to high carbon coke (Porter, 1924). Two types of plants used coal carbonization. These include plants that were primarily in the business of making coke and plants that were operated for the purpose of gas production. Though the process was similar at both facilitates, coke plants tended to be larger and sold the coal gas to gas companies for distribution (Harkins et al., 1988).

Carburetted water gas and oil gas both relied on oil for their illuminating power. The production of carburetted water gas took place in two steps. First, either coke or coal, preferably coke, was heated in the presence of steam to produce a stream of hydrogen and carbon monoxide, known as water gas. Next, oil was sprayed into this gaseous mixture, increasing the BTU capacity of the gas and creating carburetted water gas. In the production of oil gas, oils alone were heated and cracked to produce a mixture of mostly hydrogen and methane, along with other illuminates (Rhodes, 1966b).

The predominant type of gas manufactured varied over time and by region. During most of the 1800's, gas works produced primarily coal gas. Coke production was accomplished using beehive ovens, such that gas was not collected. By the late 1800's, many U.S. gas works switched to producing carburetted water gas because it was cheaper and easier to produce (Rhodes, 1966b). While in Europe, especially in Germany, the by-product coke oven was rapidly replacing beehive ovens, generating more coal gas and tar. By 1914, 100% of all German beehive ovens were replaced with by-product coke ovens, while in the U.S only 5% were replaced (Rhodes, 1966b). After the beginning of World War I, the U.S. began to aggressively build by-product coke ovens, increasing U.S. coal gas production (Porter, 1924). In 1902, the first oil gas plant was established in Oakland, California (Rhodes, 1966b). Oil gas was important in regions where coal was not easy to come by, especially the Pacific Coast region (Hamper, 2006). By 1926, the percentage of total U.S. gas manufactured from carburetted water gas plants was 58%; from coal gas plants, 35%; and from oil gas plants, 7% (Rhodes, 1966b). In Europe, carburetted water gas did not achieve the same popularity, and its used was limited primary to enriching coal gas (Thorpe, 1912).

The specific wastes generated from gas manufacturing varied depending on the type of gas produced; however, tars were one of the primary waste streams from all types of gas manufacturing. In general, tar is an opaque viscous liquid, enriched in high molecular weight compounds. The tars from coal gas manufacturing are referred to as coal tars; from carburetted water gas, as water-gas tars; and from oil gas, as oil-gas tars. All of these tars contain significant quantities of aromatic compounds (Harkins et al., 1988). Coal tar is also enriched in phenolic acids, nitrogenous bases, and ammonia (Rhodes, 1966b). Water-gas and oil-gas tars share similar characteristics. These tars are mostly absent of the acids and bases in coal tars and contain more sulfur (Rhodes, 1966b).

Tars from the same process also varied over time as technologies changed and optimal feedstocks became scarce or too expensive. Details of these changes and the implications on tar composition are provided in Table 1 for the U.S. industry. From coal gas manufacturing, tar varied somewhat predictably based on the operating temperature of the process. A lower operating temperature resulted in tars containing relatively more acids and heterocyclic compounds (Adam, 1932). Higher operating temperatures resulted in tars containing more unsubstituted aromatic compounds (Adam, 1932). Tars produced from oils were most affected by changes in the feedstock. Over time, manufacturers were forced to switch to lower quality oils based on availability and competition from other petroleum based products, resulting in heavier, lower quality tars (Rhodes, 1966b). Changes in tar quality and composition were most dramatic in water-gas tars (Rhodes, 1966b). In Germany and other parts of Europe, large quantities of brown coal were available. This type of coal was generally carbonized by low temperature methods not used in the U.S., producing a relatively low density coal tar with more tar acids and bases (Rhodes, 1945).

The ultimate fate of these tars was highly dependent upon the market conditions and the quality of the tar. Initially, coal tar use was limited primarily to wood preservation (i.e., creosote) (Harkins et al., 1988). By the late 1800's, coal tar became an important commodity, used in the synthesis of an incredible array of materials, including: dyes, perfumes, explosives, pharmaceuticals, and many more (Rhodes, 1966b). Since water-gas and oil-gas tars typically did not contain large amounts of anthracene, their usefulness was more limited (Harkins et al., 1988). Light water-gas tars were used mostly for fuel and road construction. Heavy water-gas and oil-gas tars were more difficult to use in these applications due to variable chemical compositions and higher viscosities (Rhodes, 1966b). Tars that were not sold to refiners were either landfilled or disposed of in open pits (Murphy et al., 2005).

One of the most significant hurdles to using tars was the presence of difficult to break tar-water emulsions. Refiners would only purchase tars with <3% water (Hamper, 2006). For coal tar, this was typically not a significant issue as it contained very low amounts of water that could easily be removed. As described in Table 1, carburetted water gas and oil gas producers had considerable problems with emulsions, especially after switching to heavier, lower quality oils (Hamper, 2006; Murphy et al., 2005). These emulsions were intractable, and attempts to dewater them were expensive. There were also many years after World War II when the demand for tar was low, leaving large volumes unused (Murphy et al., 2005).

Estimates for the number of specific U.S. FMGP sites vary widely from 1,500 to 50,000 and are a function of the type of facilities considered (Harkins et al., 1988; U.S. EPA, 2004). The first survey conducted by EPA identified approximately 1,500 sites, which mostly included facilities that were members of gas associations (Eng, 1985; Murphy et al., 2005). Higher estimates are obtained by considering the wide variety of facilities that used coal or coal tar. (Hatheway, 1997; U.S. EPA, 2004). Regardless of the exact number of sites, a large amount of tar was produced from gas manufacturing. Eng (1985) estimated 11.5 billion gallons of tar were produced in the U.S. from 1820 to 1950.

Given the materials and waste handling in use while these sites were in operation, U.S. EPA (2004) concluded that releases of tar and other wastes to the environment occurred at over 90% of sites. Many sites operated for over 50 years before tar was widely utilized for other products. Waste tars and tar emulsions were often mixed with subsurface materials and landfilled (Murphy et al., 2005) or disposed of in large pits (Harkins et al., 1988). Even when tars were recycled for other uses, they were typically stored in underground enclosures made of either wood, masonry, or concrete, known as tar wells (Harkins et al., 1988; Murphy et al., 2005). Over time, even a small percentage of tar leaking from a tar well could result in many thousands

of gallons released to the subsurface. Upon decommissioning, wastes in tanks and holding pits were often left in place and covered with fill (Murphy et al., 2005).

3 Composition

Tars are a complex mixture of a large number of mostly organic aromatic compounds. During the late 1800's and early 1900's, a considerable amount of work was done to isolate and identify the components of tars, especially coal tars. This interest was driven by a desire to find compounds of economic value, along with an optimism that any compound could be found in tar (Weiss and Downs, 1923). According to Weiss and Downs (1923), the authoritative work by George Lunge, entitled *Coal Tar and Ammonia*, details some 200 substances isolated from coal tar (Lunge, 1916). Rhodes (1945) published a list of 348 compounds in coal tar.

Early efforts to quantify individual constituents in tar demonstrated that most were not present at appreciable concentrations. Weiss and Downs (1923) conducted a large-scale distillation of 10,000 gallons of coal tar. As was generally accepted, this work confirmed that naphthalene was the most abundant compound, an aromatic hydrocarbon consisting of two fused benzene rings. Despite their efforts, only one compound was identified that was not previously recognized for its abundance in tar, phenanthrene. In Table 2, their results are presented along with some limited data for water-gas tars. Historically, less effort was expended to determine the composition of water-gas and oil-gas tars; however, they are expected to contain a similar list of compounds as coal tars, absent the tar acids and bases (Harkins et al., 1988).

Most of the early characterization of tars used tests to infer the chemical composition, rather than quantification of individual compounds. Based on its commercial value and abundance in tar, the only compound typically quantified was naphthalene. Other common analyses included: distillation tests, used to determine the percentage of mass in certain boiling point ranges; solubility tests, used to determine the percent mass that is either soluble or insoluble in a particular solvent; and chemical reactivity tests, used to determine the concentration of various chemical classes, such as tar acids and bases (Abraham, 1922). In Table 3, data on the characterization of U.S. tars are presented using some of the typical analyses conducted in the early to mid 1900's.

As discussed in §2, the composition of tars is a function of the gas manufacturing process from which they were produced. The data in Table 3 further illustrates the differences between various coal, water-gas, and oil-gas tars. For example, the percentage of naphthalene is greater in the coal tars produced at the greatest temperatures, namely horizontal retort and coke oven coal tar. Based on the distillation data, these tars are composed mostly of compounds with boiling points above 355°C. This fraction is the solid residue remaining after distillation and is commonly referred to as pitch (McNeil, 1964). The water-gas and oil-gas tars are almost completely absent of tar acids. In comparison, low-temperature tars produced in Germany contained from 20–50% tar acids (Abraham, 1961). There is also an interesting similarity between the tars. The sulfonation residue, which is a measure of saturated hydrocarbons (Abraham, 1922), indicates that > 90% of the mass in all the tars is of an aromatic nature. This is also true of low temperature tar (Abraham, 1961).

Using modern analytical techniques, we are still limited in our ability to fully characterize tars, in which the total number of compounds has been estimated as high as 10,000 (NIOSH, 1977). This is especially true of the pitch fraction, which can account for as much as 70% of tar mass (See Table 3). The routine state of the science of gas chromatographic analyses of PAH's typically quantifies compounds with boiling points up to approximately 500°C and as many as six aromatic rings (Poster et al., 2006). Recently, more sophisticated methods have indicated the presence of compounds with as many as 210 rings in the pitch fraction (Morgan

et al., 2008). One significant limitation in analyzing these complex compounds is the lack of reference standards (Fetzer and Kershaw, 1995).

Despite limitations, modern analytical techniques allow for considerably more detailed analysis compared to the era of gas manufacturing. Given that the coal carbonization industry continues today, the recent literature includes analyses of fresh coal tars. Some of this work continues the search for identifying chemical constituents in tars (Zhang et al., 1992; 1997). A fresh coke oven coal tar has also been used to study the fate of tar constituents in groundwater (Eberhardt and Grathwohl, 2002). Newly produced high temperature coal tars are likely to be similar in composition to those produced at U.S. FMGP's, which were virtually all high temperature tars (Rhodes, 1945). Even in the early 1900's, it was well documented that the composition of high temperature tar was mostly independent of the original coal (Porter, 1924). A relatively recent analysis of eight U.S. high temperature coal tars confirmed this observation (Novotny et al., 1981). Conversely, the composition of tars produced at low temperatures is highly influenced by the composition of the original coal (Rhodes, 1945).

Regardless of the improvement in analytical methods, there are few analyses of FMGP tars reported in the recent literature. Most site investigations of FMGP's are driven primarily by the desire to determine the extent of contamination, and tar samples are not typically analyzed (GRI, 1987). The most detailed survey of tar samples was conducted by the Electric Power Research Institute (EPRI) and included tars from eight FMGP sites (EPRI, 1993). A more recent survey analyzed 11 tars from 10 FMGP sites (Brown et al., 2005); however, this data is somewhat less useful for evaluating the impact of aging because the gas manufacturing history of the sites and the nature of the sample location is not provided (e.g., near ground surface versus well samples).

Several other tar samples have been recovered from U.S. FMGP's in order to study phenomena that influence the fate of tars in the subsurface, such as mass transfer and wettability. A number of researchers have studied two samples of flowing tars obtained from wells at FMGP's in Stroudsburg, PA and Baltimore, MD (Peters and Luthy, 1993; Luthy et al., 1993; Ramaswami et al., 1994; 1997; 2001; Ghoshal et al., 1996; Nelson et al., 1996; Powers et al., 1996; Barranco and Dawson, 1999). An additional well sample was obtained from an unspecified mid-Altantic FMGP (MacKay and Gschwend, 2001). Samples have also been studied that were obtained from holding tanks at FMGP's in Connecticut, Pennsylvania, and New York (Powers et al., 1996; Zheng and Powers, 1999; 2003; Zheng et al., 2001; Hugaboom and Powers, 2002). Only the three tars obtained from wells were analyzed for chemical constituents (Peters and Luthy, 1993; Ghoshal et al., 1996; MacKay and Gschwend, 2001).

In Table 4, compositional data from fresh coal tars is compared to tars recovered from FMGP's. The samples from the EPRI survey include liquid samples from free flowing tar plumes and holding tanks. Though the focus of this review is on the behavior and fate of tar DNAPLs in the saturated zone, data for solid tar samples collected from at or near ground surface are provided in Table 5, to give some perspective on tar aging. Though in some cases other compounds were quantified, the tables were limited to include U.S. EPA priority pollutant monocyclic aromatic hydrocarbons (MAH's) and PAH's. Two branched naphthalenes were also included, which are not on U.S. EPA's list of 16 priority pollutant PAH's but are often quantified due to their relatively high concentrations. Heterocyclic compounds and metals were limited to those detected at the highest concentrations.

The type of tar is also provided in Tables 4 and 5, which is based on historic manufacturing data. For sites in the EPRI survey with more than one type of manufacturing, the primary method is provided. As noted in §1 the tar from Stroudsburg is a water-gas tar, despite often being referred to as coal tar. The tar from Baltimore is also referred to in the literature as a coal

tar (Barranco and Dawson, 1999); however, data compiled by Eng (1985) indicates that this site produced primarily water-gas from 1890–1950.

3.1 Organic Compounds

In general, the concentrations reported in the fresh coal tar samples are similar to those reported in the historic literature. Specifically, the concentrations of the priority pollutant MAH's and PAH's reported in the fresh samples are all within two times the values reported in the historical data in Table 2. Assuming that lower MAH or PAH concentrations are indicative of tar weathering, the well samples appear to be the least weathered, while the samples taken at the ground surface are generally the most weathered. Though coal tars produced in vertical retorts would have lower concentrations of aromatic compounds regardless of weathering, they would also have a relatively low viscosity. Since the holding tank samples are viscous liquids and the surface samples are all solids, we can rule out these samples originating from vertical retorts.

Weathering of tar samples is also expected to change relative the composition of tar samples, as lower molecular weight compounds are lost first to either dissolution or volatilization and higher molecular weight compounds would actually increase in concentration. Interestingly, in all but two of the samples, naphthalene remains the most dominant compound. In the Stroudsburg sample, the branched naphthalenes are the most dominant and the distribution of the remaining compounds is similar to the other well samples. In one sample taken from the ground surface, not only is phenanthrene the most dominant compound, but other high molecular weight compounds are also seemingly enriched, such as benzo(a)pyrene. In the tar samples analyzed by Brown et al. (2005), naphthalene has the highest concentration in every sample.

Also shown in Tables 4 and 5 are several heterocyclic compounds. Heterocyclic compounds consist of ring structures in which a carbon atom has been substituted with nitrogen, sulfur or oxygen. Historically, these compounds were considered major components of low temperature coal tars, like those produced in Germany. Thus, it is somewhat surprising that these compounds are detected in U.S. coal tars and water-gas tars, albeit at concentrations one to two orders of magnitude lower than naphthalene. Compared to MAH's and PAH's, these compounds are more difficult to determine analytically (Johansen et al., 1996), but, according to some authors, are a concern in groundwater at FMGP's due to their high water solubility and toxicity (Pereira et al., 1983;Zamfirescu and Grathwohl, 2001). Unlike the MAH's and PAH's, the heterocyclic compounds do not appear to have any trends in concentration related to the degree of weathering.

3.2 Inorganic Compounds

Tars also contain a number of inorganic compounds. A number of trace metals, along with cyanide, were measured as part of the EPRI survey (EPRI, 1993). Samples were digested into acid prior to trace metal analysis using inductively coupled plasma emission spectroscopy. This is necessary in order to determine the metal concentration; however, these data do not reveal any information about the possible form of the metal (e.g., elemental vs. metal–organic complexes). The three metals with the highest concentrations are shown in Tables 4 and 5. There appears to be a slight decrease in arsenic in the holding tank and surface samples, while chromium and lead have much higher concentrations. Assuming that the holding tank and the surface samples are relatively more weathered, these data suggest that arsenic is present in a water-soluble form, while chromium and lead are present in relatively insoluble forms. Cyanide concentrations were also highest in the holding tank and surface samples.

From historical data, all tars generally contained some amount of water, which was removed mostly by gravity separation (Harkins et al., 1988). In water-gas tars, the amount of water could

be as high as 90% (Harkins et al., 1988). Coal tars were most easily dehydrated, resulting in 0–5% remaining water (Harkins et al., 1988). As noted in Table 1, intractable emulsions were common in water-gas and oil-gas tars when heavier oils were used in gas manufacturing. Thus, it is not surprising that both Brown et al. (2006) and the EPRI survey reported that several samples of tar contained high concentrations of water. In Brown et al. (2006), the water contents of three tars were less than 1%, while the remaining eight tars contained from 22–55% water. One study suspected the water content was a sampling artifact (EPRI, 1993), while the other speculated it was the result of tar aging (Brown et al., 2006). Given the significant problems the gas industry experienced with tar-water emulsions, combined with the lack of market value for these materials, these samples could also be emulsions.

3.3 Saturates, Aromatics, Resins, and Asphaltenes

Characterization of tars using solubility tests has been practiced since the early days of gas manufacturing. As early as 1837, the solubility in light petroleum naphtha was used to separate asphaltenes, the insoluble fraction, from malthenes, the soluble fraction (Abraham, 1961). Historic data for coal tars indicate that the asphaltene content is highest in higher temperature tars. Specifically, the percentage of asphaltenes in coal tar produced in vertical retorts ranged from 20–40%; in coke ovens, 25–40%; and in horizontal retorts, 60–80% (Abraham, 1961).

SARA analysis is a more modern technique, related to the petroleum naphtha solubility test, which is used to separate mixtures into four general classes, including: saturates, aromatics, resins, and asphaltenes (Kharrat et al., 2007). Asphaltenes have more recently been defined as the fraction insoluble in either n-pentane or n-heptane (Hanson, 1964), a definition which continues to be used today (Kharrat et al., 2007). The remaining fractions are separated using column chromatography based on increasing polarity, resins being the most polar. The exact composition of resins and asphaltenes is not known, but it is a topic of considerable research in the petroleum literature. These high molecular weight compounds are believed to play an important role in changing wettability, which affects petroleum recovery. (Speight, 1999; Buckley and Wang, 2002; Xie et al., 2002; Drummond and Israelachvili, 2004).

In Table 6, the composition of crude oil is compared to that of several FMGP tars. The asphaltene content of three FMGP tars was over twice as much as an average heavy crude oil. These high asphaltene contents are consistent with the historic data; however, given that accurate and reproducible determination of asphaltenes depends on the quality of the solvent (Fan and Buckley, 2002), comparing these results to data from several decades ago must be done with caution. Even in the recent literature, the methods used to isolate these fractions often vary. For example, Haeseler et al. (1999) isolated saturates, aromatics, and resins by extracting with cyclopentane, possibly biasing their results.

4 Physicochemical Properties

The physicochemical properties of complex mixtures are a function of their chemical composition. Historical tests of tar properties include specific gravity and the viscosity (Abraham, 1922). More current analyses also typically include the average molecular weight ($\overline{Mw}$), which is required for estimating equilibrium concentrations using Raoult's law (See §5.1). In order to determine the distribution and movement of NAPLs in porous medium systems, it is also critical to have an understanding of interfacial phenomena, which are a function of IFT, wettability, and the capillary pressure history of the system.

4.1 Specific Gravity and Viscosity

In Table 7, historic specific gravity and viscosity data are provided for several tar samples from each major category of gas manufacturing in the U.S. In the early 1900's the standard

temperature for determining specific gravity was 15.5°C (Weiss, 1915). As noted in Table 7, data at 25°C were converted to the standard temperature using the method of Weiss (1915), resulting in <1% increase in the specific gravity. Viscosity of tars is considerably more sensitive to temperature changes (Traxler, 1964;Brown et al., 2006). Besides the influence of temperature, comparing tar viscosity reported in the early 1900's is further complicated by methods that often used arbitrary units of measure (Traxler, 1964). During the mid 1900's, numerous consistency relationships were developed to allow for the comparison between various methods (Traxler, 1964). A set of relationships, developed based on coal tars, was used to estimate the dynamic viscosity at 35°C in Table 7 (Phelan and Rhodes, 1966). Due to the complexity of tar, no methods are available to convert tar viscosities to values corresponding to typical subsurface temperatures (e.g., 10°C).

These data further illustrate variations in tar properties with changes in the gas manufacturing process. Overall, the specific gravity varies from 1.061 to 1.334. There is considerable overlap among each major category of tar; however, the specific gravity is generally lowest in the water-gas tars and highest in the oil-gas tars. For coal tars, increases in the specific gravity are positively correlated to the temperature of the specific process. For water-gas tars, there is a significant increase in the specific gravity for tars produced using heavy oils. For oil-gas tars, the data illustrate changes in specific gravity due to both temperature and feedstock changes. As shown in Fig. 1, viscosity is positively correlated with specific gravity and varies widely from ~10–1,000,000 cP.

In Table 8, the $\overline{Mw}$, specific gravity, and dynamic viscosity, are provided for several coal tars recovered from FMGP's and one fresh coal tar. In general, the tars with the lowest PAH concentrations have the highest specific gravity and viscosity. Along with the data for $\overline{Mw}$, this trend is consistent with the understanding that the fraction we are unable to quantify is composed of high molecular weight compounds.

For the most part, the property data in Table 8 are consistent with the type of gas manufactured. For example, the tars from Stroudsburg and Baltimore both have low density and viscosity, which are consistent with water-gas tars, as shown in Fig. 1. The tar from Pennsylvania also appears to be a water-gas tar. For the liquid samples in the EPRI survey, the property data are also consistent with the predominant type of gas manufactured. For the weathered solid samples, the specific gravities are higher than any reported in the historic data provided in Table 7.

Another consideration in the measurement of viscosities is the possibility that these materials could exhibit non-Newtonian behavior, such that viscosity is also a function of the applied shear stress. Non-Newtonian behavior has been documented for coal tar pitches (Yanovsky et al., 1988; Li and Li, 1996). For coal tars, studies of rheological behavior have generally revealed Newtonian flow, but they have been conducted at temperatures > 100°C (Traxler, 1964). The behavior of these materials has not been assessed at lower temperatures and sheer stresses where non-Newtonian behavior is more likely (Traxler, 1964).

4.2 Interfacial Tension

The IFT between tar and water is generally considered low when compared to other DNAPLs; however, it has only been measured for a small number of samples. In Table 9, IFT's are listed along with the corresponding pH. The data show that IFT's at neutral and acid pH vary from 20–25 dynes per centimeter. At higher pH, the IFT decreases to near zero. The dependence of IFT on pH is believed to be controlled by the acid functional groups contained in asphaltenes (Barranco and Dawson, 1999; Zheng and Powers, 2003). As noted, the properties of the Stroudsburg, Baltimore, and Pennsylvania tars are at the low end of the reported range. Given

the variable composition and wide range of properties for FMGP's tar, it is possible that the range of IFT's could be much broader than what is listed here.

4.3 Wettability

In NAPL contaminated porous media, it is important to understand the wetting behavior of liquid phases. The wetting phase coats the solid medium while the non-wetting phase tends to exist as isolated globules at residual saturation occupying the largest pore openings. Wettability is defined as the attraction of a liquid phase to solid surface, and it is typically quantified using a contact angle with the solid phase. NAPL contaminated systems can be water wet, oil wet, or exhibit mixed wettability. Changes in wettability from water to oil wet have significant impacts on the pressure-saturation relationship and make remediation particularly challenging.

The ability of coal tar to alter the wettability of solid media has been verified using bottle tests. Bottle tests were originally developed to test the wetting behavior of crude oil-water systems (Dubey and Doe, 1993). Crude oils are well documented for altering wettability. The bottle test is a qualitative way to assess system wettability. It involves shaking a mixture of water, NAPL, and unconsolidated media over a period of time to observe the distribution of phases. Powers et al. (1996) used the bottle test to compare the wettability for a variety of NAPLs including neat solvents, which remained water wet (e.g., TCE); petroleum products, which were mostly weakly-water wet or mixed wetting (e.g., gasoline and crude oil); and coal-derived creosote and tar, which were both oil wet.

Asphaltenes contain organic bases that are believed to cause these wettability shifts (Barranco and Dawson, 1999; Zheng et al., 2001). In bottle tests, Powers et al. (1996) used dodecylamine as a surrogate compound to illustrate how increasing the amount of an organic base in a NAPL changes wettability from strongly water wet to oil wet. At low pH, these organic bases become positively charged and have an even stronger attraction to solid grains, which are typically negatively charged. Zheng and Powers (1999) conducted bottle tests with four tars and four creosote samples at pH of 7.2 and 4.7. At neutral pH, only one tar and one creosote were wetting. At the lower pH, all the creosotes and half the tars were wetting. Zheng and Powers (1999) also showed that NAPLs with higher base numbers were more likely to be the wetting phase. Base numbers were determined using non-aqueous titrations and correspond to the milligrams of acid required to neutralize one gram of tar. Of the four tar samples analyzed, the one with the highest base number exhibited oil wetting behavior regardless of pH.

A more quantitative measure of wettability is the contact angle. Contact angles are measured by placing a drop of a liquid, though a syringe, on a flat, clean surface and measuring the angle between the two. For NAPLs in porous medium systems, researchers typically immerse a drop of NAPL in an aqueous phase on a solid media (e.g., quartz slides) and measure the angle through the water phase (Mayer and Hassanizadeh, 2005). Contact angles can be determined as the drop is created, the advancing contact angle; once the system has reached equilibrium, the static contact angle; and as the drop is withdrawn, the receding contact angle. The contact angle, θ, is related to interfacial tension, γ, by Young's equation, such that

$$\gamma^{ns} - \gamma^{ws} = \gamma^{nw} cos(\theta) \quad (1)$$

where s is the solid phase, n is the NAPL phase, and w is the aqueous phase. Water-wet materials have contact angles less than 90°, and oil-wet materials have contact angles greater than 90° (Bear, 1972). The transition from water to oil wet is referred to as intermediate wetting, the range for which is generally considered to be between 62–133° (Morrow, 1976).

Films at the NAPL-aqueous phase interface appear to strongly influence contact angle measurements. In Powers et al. (1996), equilibrium contact angle measurements for coal tar on quartz were attempted, but not reported, due to the presence of films interfering with these measurements. Barranco and Dawson (1999) measured static, advancing and receding contact angles for solutions of varying pH, from 3.4–12.4. The static and advancing contact angles were almost constant and below 20°, indicating a water-wet system. However, the receding contact angles varied with pH, averaging approximately 175°, from pH 3.4–6.7; steadily decreasing, from pH 6.7–8; and averaging approximately 10°, from pH 8.0 and above. When the receding contact angle indicated oil-wet conditions, a film was also present on the surface of the tar, which adhered strongly to the quartz surface. Zheng et al. (2001) also measured receding contact angles and showed similar changes in wettability with pH, as well as with increasing asphaltene concentration.

4.4 Capillary Pressure

The contact angle and the interfacial tension both affect the mobility of NAPL through porous media. The relationship is expressed quantitatively at the microscale using the Laplace equation, which relates the capillary pressure, P_c, to the interfacial tension and contact angle as

$$P_c = \frac{2\gamma^{nw}\cos\theta}{r}, \tag{2}$$

where r is the average radius of curvature (Corey, 1994). For many environmentally relevant NAPLs such as, PCE and TCE, P_c is controlled primary by the interfacial tension. For tars, the interfacial tension is much lower, and the contact angle or wettability is likely to also play an important role in the P_c (Barranco and Dawson, 1999; Zheng et al., 2001).

The work of adhesion has also been used to understand the relative importance of interfacial tension and wettability, which, in this case, is the work required to separate the NAPL from the solid and is given by (Mack, 1964)

$$W^{ns} = \gamma^{nw}(1 - \cos\theta). \tag{3}$$

Dong et al. (2004) concluded that W^{ns} was driven primarily by the coal tar-interfacial tension rather than contact angle; however, their assessment was based on the static contact angle, which indicated water to weakly-water wetting behavior. As discussed in § 4.3 the static and receding contact angles are very different in tar systems. In Dong et al. (2004), photographs of both static and receding NAPL drops are provided. While the static case has a contact angle < 90°, the receding case has a contact angle > 90°, indicating oil wetting behavior.

5 Process Modeling

In order to understand the risks posed by tars in the subsurface, we must be able to estimate the dissolution of individual chemical species. This requires an understanding of both equilibrium concentrations and the amount of time required to reach equilibrium, or the rate of mass transfer. Because the individual species in tars have different solubilities, the overall chemical composition of the NAPL phase can change over time. This can lead to instabilities in tar mixtures, such that some compounds may begin to precipitate within the NAPL phase. The following sections describe the approaches taken in the literature to model these processes.

5.1 Equilibrium Dissolution

In general, the aqueous phase concentration for an individual chemical species in equilibrium with tar will be less than the solubility for the pure species; however, the exact relationship between aqueous and tar phase concentrations is not completely understood. Some researchers have described the equilibrium dissolution from a NAPL phase empirically using a partition coefficient, K_{nw_i}, defined as

$$K_{nw_i} = \frac{C_i^n}{C_{ei}^a} \tag{4}$$

where C_i^n is the concentration of the i^{th} species in the NAPL phase and C_{ei}^a is the equilibrium concentration of the i^{th} species in the aqueous phase (Lee et al., 1992; Endo and Schmidt, 2006). A common approach in environmental chemistry is to relate a compound's octanol-water partition coefficient, K_{ow}, to the partition coefficient in a more complicated NAPL (Schwarzenbach et al., 2003). Endo and Schmidt (2006) developed the following regression equation for coal tar-water systems from a survey of literature data

$$\log K_{nw_i} = 1.16 \log K_{ow_i} - 0.19. \tag{5}$$

Using this relationship, we can estimate the log K_{nw} for any chemical that has a known log K_{ow}; however, this approach does not account for the variability among tars that may affect partitioning.

A more rigorous approach to predicting equilibrium concentrations based in thermodynamics is Raoult's law (Schwarzenbach et al., 2003). This approach relates C_{ei}^a to the species' subcooled pure liquid solubility, S_i, and mole fraction in the nonaqueous phase, χ_i^n, such that

$$C_{ei}^a = \chi_i^n S_i. \tag{6}$$

By definition, the mole fraction for the i^{th} species is the ratio of the moles of i, m_i, to the total number of moles. Since the entire composition of these complex mixtures is not known, the mole fraction is typically calculated as follows,

$$\chi_i^n = \frac{m_i}{\sum_{i=1}^{n} m_i} = \frac{C_i^n \times \overline{Mw}}{10^6 \times Mw_i}, \tag{7}$$

using the concentration of species i in the NAPL phase, C_i^n (mg/kg); the molecular weight of the species, Mw_i; and the average molecular weight of the NAPL, $\overline{Mw}$. The subcooled pure liquid solubility is determined by

$$S_i = \frac{C_{si}^a}{(f^S/f^L)_i}, \tag{8}$$

where C_{si}^a is the solubility in the aqueous phase of the single species *i* neglecting composition effects and $(f^S/f^L)_i$ is the solid to liquid fugacity ratio. For compounds that are liquids at ambient conditions, $(f^S/f^L)_i$ is one, reducing Raoult's law to

$$C_{ei}^a = \chi_i^n C_{si}^a. \tag{9}$$

Theoretically, a compound in a NAPL mixture consisting of like compounds, should adhere to Raoult's law. If a compound is in a mixture of compounds with very different properties, deviations from ideal behavior can occur (Schwarzenbach et al., 2003). In a non-ideal mixture, C_{ei}^a is expressed as

$$C_{ei}^a = \gamma_i^n \chi_i^n C_{si}^a, \tag{10}$$

where γ_i^n is the activity coefficient for species *i* in the NAPL phase.

In Fig. 2, we plotted experimentally determined values for C_{ei}^a versus predicted values calculated based on Raoult's law for several tar samples. Predicted values for C_{ei}^a require the $\overline{Mw}$ for the NAPL phase. The traditional method of determining $\overline{Mw}$ is vapor pressure osmometry (VPO), which can be prone to error due to high solids content and viscosity (Brown et al., 2005). In Fig. 2, predicted values were calculated using either experimentally determined $\overline{Mw}$ (Fig. 2a) or best fit values for $\overline{Mw}$ using the method described by Brown et al. (2005) (Fig. 2b). Brown et al. (2005) concludes that using fitted values for $\overline{Mw}$ is more appropriate given the ultimate use of the data (i.e., predicting C_{ei}^a using Raoult's law). While this may be true, several chemicals in Fig. 2 continue to have deviations from the ideal prediction exceeding a factor of 2, even when the fitted $\overline{Mw}$ is used.

Deviations from Raoult's law could be due to non-ideal behavior, analytical limitations, or uncertainty in chemical properties. Thermodynamic modeling has been conducted to estimate activity coefficients for several tars, including the Stroudsburg tar (Peters et al., 1999b). MAH's generally had activity coefficients slightly less than 1 (e.g., 0.8), and most PAH's had activity coefficients at or near 1. Their analysis did not include tars with more polar constituents (e.g., phenols), which are more likely to deviate from Raoult's law (Endo et al., 2008). In terms of analytical methods, the analysis of PAH's is generally considered somewhat standard; however, special care must be taken to quantify accurately individual compounds in complex mixtures (Schmid and Andersson, 1997). Measuring aqueous phase concentrations of PAH's can also be confounded by losses in sample preparation, including volatilization, photodegradation, and sorption. Finally, there is also some uncertainty due to chemical properties, such as the subcooled liquid solubility (Peters et al., 1997).

Higher molecular weight PAH's, such as benzo(a)pyrene, are a particular concern from a risk perspective due to their relatively high toxicity and possible increased mole fraction as tar ages (Peters et al., 1999a); however, little data is available to evaluate the dissolution behavior of these compounds. The range of molecular weights for all the priority pollutant PAH's is from 128–278 g/mol, with benzo(a)pyrene having a molecular weight of 252 g/mol. In Lee et al.

(1992), equilibrium aqueous phase concentrations were reported for compounds with a molecular weight up to 228 g/mol. In Brown et al. (2005) close inspection of data plots reveal that equilibrium aqueous phase concentrations were not determined for PAH's with a molecular weight > 202 g/mole. Though not explicitly discussed by either author, it is likely that the aqueous phase concentrations of higher molecular weight compounds were less than the analytical detection limit. In Lee et al. (1992), the most significant deviations from Raoult's law were for the highest molecular weight compound measured, benzo(a)anthracene (i.e., 228 g/mol), such that measured concentrations were consistently less than expected. These deviations were attributed to analytical limitations (Lee et al., 1992).

5.2 Mass Transfer

Mass transfer from a NAPL to an aqueous phase is generally described by a linear driving force model of the following form

$$\overset{in\rightarrow ia}{M} = \varepsilon^{na} k_{ai} (C_{ei}^{a} - C_{i}^{a}) \tag{11}$$

where C_i^a is the aqueous phase concentration, k_{ai} is a mass transfer coefficient, and ε^{na} is specific interfacial area between the NAPL and aqueous phases (Miller et al., 1990). Since the interfacial area is typically unknown, mass transfer is often characterized in terms of the lumped mass transfer rate coefficient

$$K_{ai} = \varepsilon^{na} k_{ai}. \tag{12}$$

For single species NAPLs, a considerable body of work exists on determining the parameters affecting the mass transfer rate in porous media. Due to the complex nature of these systems, several empirical relationships have been derived to predict mass transfer using non-dimensional parameters (Miller et al., 1990; Geller and Hunt, 1993; Imhoff et al., 1994; Powers et al., 1994; Kim and Chrysikopoulos, 1999). Though these empirical relationships may successfully predict mass transfer for a set of experimental data, mass transfer is fundamentally a function of the microscale morphology and topology of the NAPL-aqueous phase interface, and several other properties. Recently, microscale simulations have been successfully used to predict macroscale mass transfer; however, there is considerable work that needs to be done for a complete understanding of this complicated process (Pan et al., 2007).

For multi-species NAPLs such as tars, mass transfer is further complicated by several factors. One obvious complication is that the composition of the NAPL itself can change over time. Changing composition may affect other physical parameters such as viscosity and density. Within the NAPL phase, varying rates of molecular diffusion or diffusional drag of individual species may limit dissolution and lead to changes in NAPL composition in both space and time (Miller et al., 1990; Holman and Javandel, 1996; Brahma and Harmon, 2003). Our ability to understand mass transfer is also limited by uncertainties in the equilibrium concentration and possible deviations from Raoult's law. Finally, the changing composition of tars may also lead to some species precipitating within the NAPL phase (See §5.3).

For tars, few experiments have been conducted to determine mass transfer rates. In flow-through and batch mass transfer experiments using coal tar imbibed into a porous medium consisting of small diameter silica particles, the lumped mass transfer coefficients for naphthalene and phenanathrene decreased over a two to three hour time frame (Ramaswami et al., 1994; Ghoshal et al., 1996; Ramaswami et al., 1997). This decrease was speculated to

be a result of interfacial films forming at the water-NAPL interface; however, experiments with larger diameter glass beads and coal tar globules did not exhibit the same behavior (Ghoshal et al., 1996; Ramaswami et al., 1997).

Some evidence suggests that the mass transfer coefficient may not vary much between different PAH's. Mass transfer coefficients were determined for various synthetic mixtures of toluene and eight PAH's with molecular weights from 128–202 g/mol (Mukherji et al., 1997). The coefficients varied from 0.8×10^{-3}–3.0×10^{-3}. Mass transfer coefficients also tended to increase for high molecular weight compounds, yet this increase was attributed partly to analytical artifacts. In the synthetic mixtures, the mole fraction of naphthalene was varied from 0.0–0.25 while the mass transfer coefficient remained essentially the same. No experiments were identified that determined mass transfer coefficients for higher molecular weight PAH's in tar, such as benzo(a)pyrene.

5.3 Precipitation of PAH's

Raoult's law has been used to predict the precipitation from tar NAPLs with some limited success. As pure compounds, many of the PAH's in tars are solids at ambient conditions. As tars age, we expect that the more soluble components will be preferentially depleted, resulting in increased mole fractions of other components. As derived by Peters et al. (1997), components of ideal liquid mixtures will be stable when

$$\chi_i^n \leq (f^S / f^L)_i. \tag{13}$$

Peters et al. (1997) compared mole fractions in a solid and liquid tar; in the solid tar, mole fractions of several PAH's exceeded $(f^S/f^L)_i$. To more definitely determine whether or not ideal behavior was likely for PAH mixtures, solid-liquid equilibria were evaluated for binary, ternary, and quaternary mixtures using naphthalene, 2-methylnaphthalene, acenaphthene, phenanthrene (Peters et al., 1997; 2000). While ideal behavior was observed for naphthalene and acenaphthene, phenanthrene and 2-methylnaphthalene appeared to co-precipitate even when solubility theory indicated only one should be forming a solid phase. Given the large number of compounds in tars, there is clearly much more work that needs to be done to understand this phenomena.

6 Remediation and Modeling

There is now a clear understanding that simple pump-and-treat approaches do not provide effective and efficient solutions for remediating FMGP sites. The methods currently used to remediate these sites can be grouped into three general categories: source-zone removal, including excavation and hauling; source-zone containment, including capping, slurry walls, sheet piling, and in-situ stabilization; and source-zone treatment, including thermal treatment, chemical treatment, and biodegradation (McGowan et al., 1996). For all of these methods, the overall goal is to reduce the mass flux from the source zone.

In terms of tar DNAPLs that have migrated into the saturated zone, excavation is not typically a viable option. At large sites, it is often possible to pump and remove the free-phase DNAPL directly (Wu et al., 2000); however, a considerable amount of mass can be left behind as trapped residual. Much effort has been focused on the use of flushing solutions intended to facilitate DNAPL removal, such as hot water and polymers (Wu et al., 2000). Initially developed for the petroleum industry, these methods can successfully remove large amounts of mass. For example, hot water injection resulted in the recovery of 1500 gallons of tar at the Stroudsburg,

PA FMGP site (Johnson and Fahy, 1997). For slow moving tar plumes, removing free-phase DNAPL can also reduce the potential for further migration.

In general, these techniques still tend to leave behind a substantial amount of entrapped residual material. Often additional efforts are necessary to reduce the mass flux from the residual phase to the mobile dissolved phase (Wu et al., 2000). It is also believed that at many sites that the majority of the tar mass is present as entrapped residual (Luthy et al., 1994). Mass removal of residual DNAPL may be achieved through mobilization or dissolution using cosolvents and surfactants. Chemical and biological treatment may also be applied. For single component NAPLs, a considerable amount of experimental work has been conducted to understand the effectiveness of these techniques at a variety of scales. For one-dimensional column experiments with relatively high residual saturations, the total mass removed is often greater than 90% (Soga et al., 2004). In larger three-dimensional experiments with lower residual saturations, the total mass removed is typically much less, ranging from approximately 30–90% (Soga et al., 2004).

The number of controlled experiments with tar DNAPLs is much more limited but provides some perspective regarding the dificulty of removing these mixtures. In Table 10, several small-scale laboratory experiments that used tar DNAPLs are summarized. Two of these experiments were conducted with high starting residual saturations that are more likely to be encountered in tar pools (Hugaboom and Powers, 2002;Giese and Powers, 2002). In both experiments, flushing solutions were tested under varying conditions of wettability. Under oil-wet conditions, the residual saturations after flushing ranged from 35–47%. Under water-wet conditions, the residual saturations were further reduced but still remained anywhere from 20–30%. Though mass flux was not determined in these experiments, it is clear from experimental results using single component DNAPLs that residual saturation must be reduced much further to achieve a meaningful reduction in mass flux (Soga et al., 2004).

In Table 10, an experiment is also summarized that used a cosolvent to enhance the dissolution of a tar DNAPL in a one-dimensional column (Roy et al., 1995). In this case, the starting residual saturation corresponded more closely to an entrapped DNAPL. The goal of this experiment was to remove the DNAPL constituents at the same rate. After 40 pore volumes, tar mass was still leaching from the column and the DNAPL remaining in the column appeared to have a much higher viscosity then the starting material. Though mass fluxes were not determined for individual chemicals, the researchers concluded that components where not dissolving at the same rates.

At sites where using chemical or physical means to remove tar is not possible, natural attenuation has become an important remedial option. Processes that contribute to natural attenuation include: dilution, dissolution, sorption, precipitation, volatilization, biodegradation, and abiotic degradation. Of these, biodegradation is the primary mechanism for natural attenuation of PAH’s (Lingle and Brehm, 2003). The ability for microorganisms to degrade PAH’s has been well documented for many decades (Mueller et al., 1989; Cerniglia, 1992; Bamforth and Singleton, 2005). It is also well documented that the presence of PAH degrading microorganisms is most likely to occur at locations of long-term persistent contamination (Cerniglia, 1992). Not surprisingly, the presence of PAH degrading microorganisms has been confirmed at several FMGP sites (Lingle and Brehm, 2003; Bakermans et al., 2002; Zamfirescu and Grathwohl, 2001; D’Affonseca et al., 2008).

For remediation via natural attenuation to be a viable option, there is often an emphasis on both confirming current attenuation of contaminants and understanding the length of time required for these processes. Thus, it is important to understand the factors controlling the biodegradation rate and considerable work is still required to understand the complex nature

of this process (Cerniglia, 1992; Bamforth and Singleton, 2005). For example, most historic studies of biodegradation used pure cultures and single compounds. Thus, there is a need to understand the biodegradation of mixtures using native cultures (Cerniglia, 1992; Bamforth and Singleton, 2005). Though there has been limited study on the biodegradation of high molecular weight PAH's, it is known that biodegradation rates tend to decrease with increasing molecular weight (Herbes, 1981; Cerniglia, 1992; Bamforth and Singleton, 2005).

One of the challenges with demonstrating natural attenuation for tars is that dissolution of individual compounds varies both spatially and temporally. This phenomena has been well documented in a long-term field study using an emplaced, immobile creosote source zone consisting of 74 kg of DNAPL premixed with sand (Fraser et al., 2008). Though creosote is a distillation product of coal tar and does not contain as wide a molecular weight distribution as coal tar, it has the same multi-component nature as other FMGP tars. The dissolution of compounds from creosote to groundwater was found to qualitatively agree with Raoult's law for 9 out of 11 compounds analyzed. Specifically, the most soluble compounds (e.g., phenol) were first to appear in groundwater and were no longer detected after a few hundred days. Compounds with intermediate solubility (e.g., naphthalene) continued to increase in concentration up to 3,000 days, after which time concentrations began to decrease. The groundwater concentrations of the compounds with the lowest solubility continued to increase after 5,000 days. For each compound analyzed, the extent and concentration of the dissolved phase plume was much less than the Raoult's law prediction, which was attributed mostly due to biotransformations.

For most FMGP sites, we would expect much larger amounts of DNAPL to have been either leaked or disposed of over time when compared to the field study described above. At a FMGP site in Germany, innovative field techniques were used to define the extent and distribution of DNAPL mass, which was closely connected to local changes in heterogeneity (D'Affonseca et al., 2008). From this analysis, it was determined that the plume contained 188 tons of DNAPL within a 50 by 100 meter footprint. Transport modeling was used to understand the time frame for natural attenuation. After 1,000 years, they estimated that the 100% of the mass would be depleted for the high solubility compounds; 40%, for intermediate solubility compounds; and only 2% for the lowest solubility compounds. Thus, for sites with large amounts of subsurface tar DNAPLs, the highest molecular weight PAH's may not begin to dissolve for several hundred years.

Field-scale modeling assessments, like the one described above, are important tools in understanding the time scales involved for natural attenuation to occur, along with the impacts further source reduction would have on that time scale. However, the uncertainty involved in such long-term estimates along with the complexity of the system being modeled cannot be overstated. The development of multiphase, multicomponent models is a substantial area of research in terms of appropriately describing these complex physical phenomena, as well as, achieving numerically accurate and computationally efficient implementations (Miller et al., 1998). Even in the case of single component models, determining source-zone mass flux has proven to be difficult (Soga et al., 2004).

In the case of multicomponent tar DNAPLs, we are faced with further layers of complexity, including the changing composition of the DNAPL in space and time and changes in system wettability. In current modeling efforts, simplifying assumptions are often required due to lack of data or computational limitations. For example, D'Affonseca et al. (2008) modeled two chemicals individually and all other chemicals were modeled using three representative chemicals. Over the long time scales that these DNAPLs exist, there is likely to be a dynamic relationship between the mobilization of DNAPL and the changing composition of DNAPL due to dissolution and precipitation. DNAPL aging will certainly increase density, possibly

causing tars with near-neutral density to sink further over time. To date, there have been several efforts to model the dynamics of multicomponent dissolution (Peters et al., 1999a; Lee, 2004; Eberhardt and Grathwohl, 2002), as well as investigations related to the migration of tar DNAPLs (Jackson et al., 2006). Little work has been done to understand the relationship between the two.

We also have almost no information on how tars might change spatially across a given site. This could be important as some tars migrate over long distances. An area of active research in the petroleum industry is related to understanding the compositional changes in crude oils as they migrate. Asphaltenes are believed to interact with the solid phase resulting in a chromatographic separation of compounds (Li et al., 1992; 1994; Larter et al., 1996; Li et al., 1997; Taylor et al., 1997; Bastow et al., 2003). In fact, investigations are on-going in the petroleum literature on how to use this phenomenon as a way of tracking the movement of crude oil (Li et al., 1992; 1994; Larter et al., 1996; Li et al., 1997; Taylor et al., 1997; Bastow et al., 2003). Given the enhanced concentration of asphaltenes in tars, it seems possible that the movement of tar could result in similar changes in composition.

7 Conclusions

Gas manufacturing was a dominant industry throughout the U.S. and Europe for over a century. Decades have passed since the recognition that tars at FMGP's are potential sources of groundwater contamination; still, significant gaps exist in our fundamental understanding of the environmental processes that govern their movement and dissolution. Without this fundamental knowledge, it is impossible to build reliable mechanistic models to assess DNAPL migration and dissolution. We are also restricted in our ability to design and implement new remediation strategies.

Considering the published literature of the last half of the 20th century, in some respects, our knowledge of the composition and properties of these tars has progressed little, and may even have been lost. Early in the history of gas manufacturing, the complex nature of tars was well recognized and widely studied, along with the influence of the type of gas manufacturing, operating conditions, and raw materials. We believe historic data is especially useful if we are able to connect tars at FMGP's to the original manufacturing process. Wider recognition of the influence of the tar origin on composition may provide future researchers an additional means of understanding the considerable variability among tar samples.

Given the variability in tar composition and properties, there is a clear need to study the properties of a wider range of tars (e.g., contact angles, interfacial tension, wettability). This is especially needed to enhance our understanding of interfacial phenomena, which plays such a key role in the fate of subsurface tars. To date, the tars that have been studied in relation to interfacial phenomena are likely water-gas tars. In coal tars, the presence of phenolic compounds could have a significant impact on interfacial phenomena.

Though some methods of characterizing the bulk properties of mixtures are still used today (e.g., SARA analysis), current analysis of tars tend to focus more on particular chemicals or groups of chemicals. Clearly, this focus is driven partly by regulation but also by continued analytical limitations. Especially notable is a lack of data on the high molecular weight PAH's in studies of equilibrium dissolution, mass transfer, and biodegradation. These compounds are also typically drivers in risk assessments; thus, an accurate understanding of their behavior is critical to assessing the future risk from FMGP's.

In general, we believe that there is a need to view these complex mixtures in a more holistic manner. On one end of the spectrum, we have studies of mass transfer and biodegradation that consider a relatively small group of PAH's. On the other end, we have studies on enhanced

remediation that make no attempt to quantify the impact on individual components and consider only the total removal of NAPL mass. In particular, we believe there should be less emphasis on the average molecular weight as a means of characterizing these mixtures. More emphasis on determining the entire molecular weight distribution is needed, along with an understanding of how this distribution changes with NAPL aging.

Interestingly, both data and modeling indicate that subsurface tars at FMGP's have aged little. Compositional data also seem to contradict our understanding of aging described by Raoult's law. Specifically, it is noteworthy that naphthalene, the most abundant and most soluble PAH in unweathered samples, is still the most abundant compound in some of the most weathered samples reported in the literature. This apparent discrepancy could be due to diffusional limitations within the DNAPL phase associated with increasing viscosity.

Improving our understanding of the factors governing the long-term fate of these complex mixtures, improves our decision making ability with regard to remedial options. A sound understanding of interfacial phenomena is especially critical for developing better methods for source-zone remediation. Understanding the potential benefits of further source-zone remediation along with the viability of natural attenuation is directly linked to this fundamental understanding, which is critical to developing better mechanistic models.

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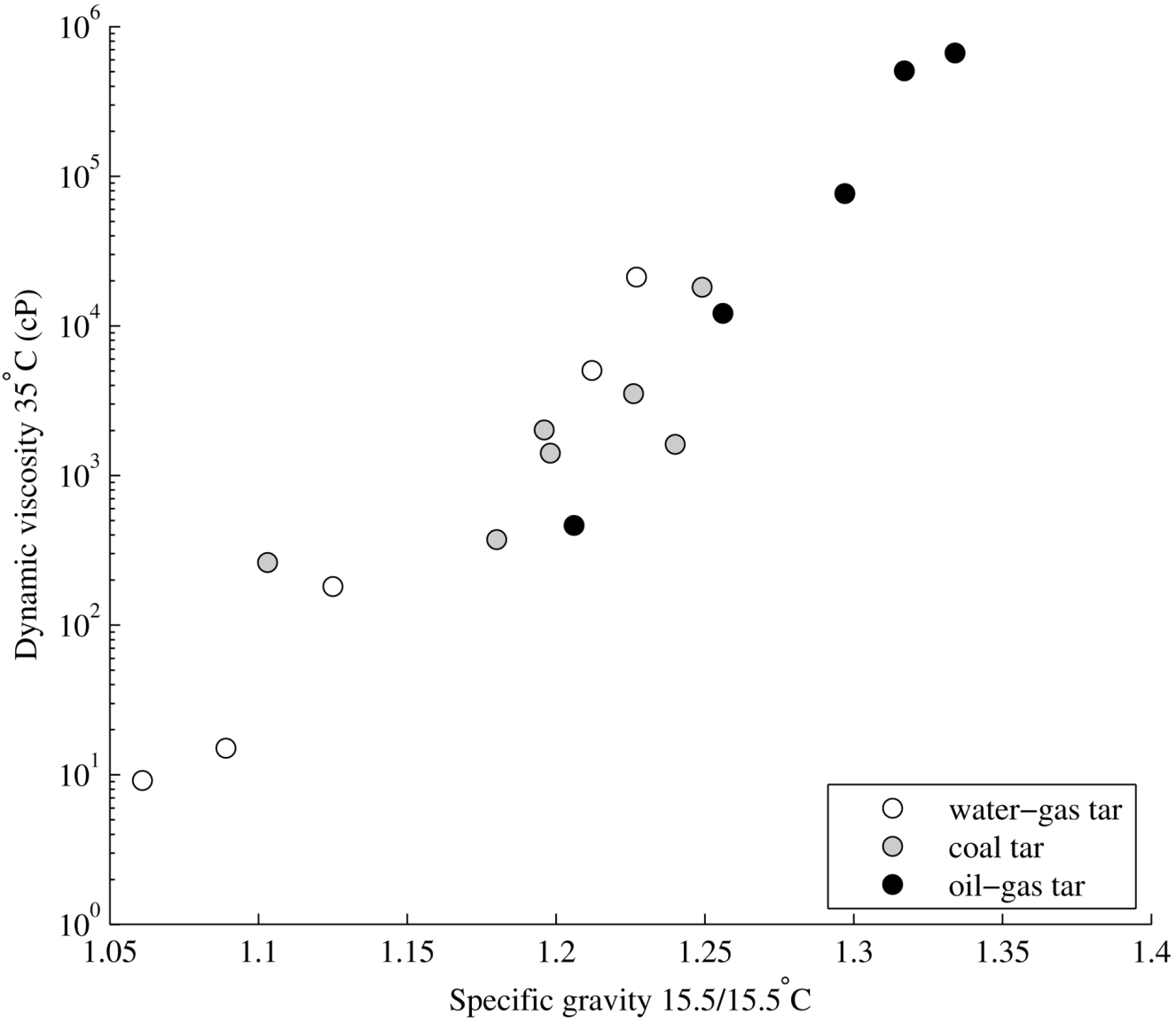

Fig. 1.
Relationship Between Tar Viscosity and Specific Gravity. Data are from Table 7.

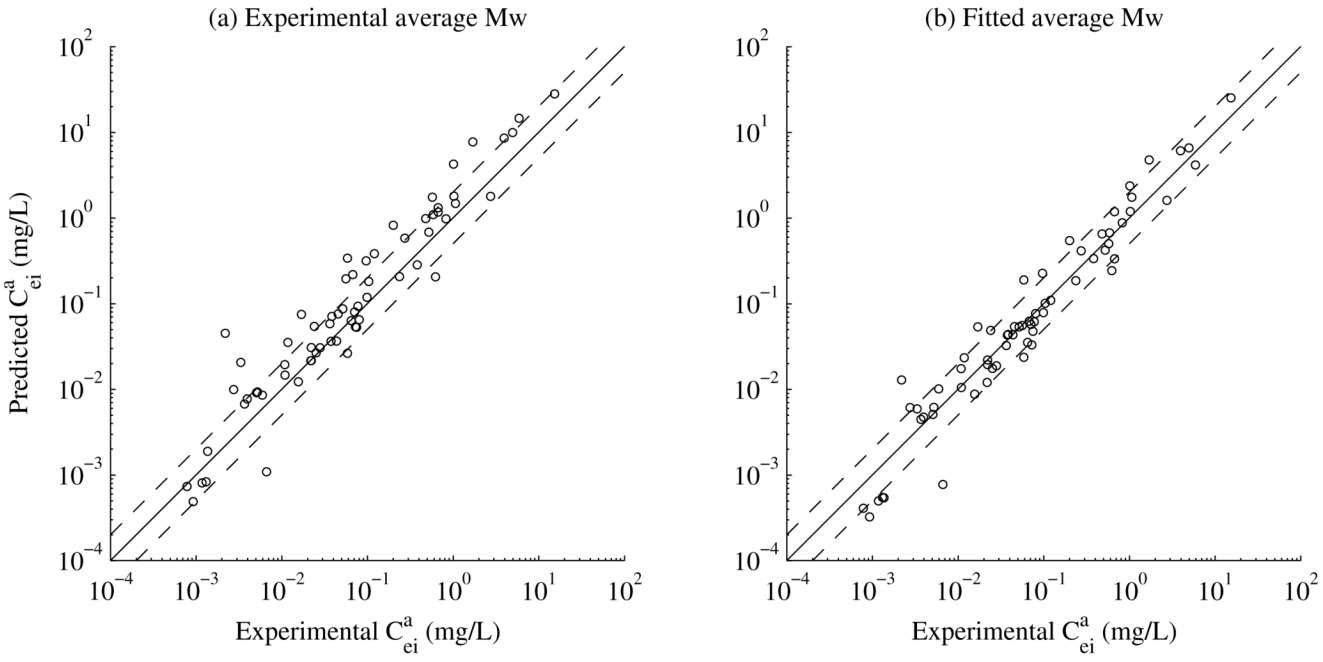

Fig. 2.

Comparison of experimental and predicted C^a_{ei}. Predicted values were calculated based on Raoult's law using either experimentally determined $\overline{Mw}$ (a) or fitted $\overline{Mw}$ (b). Values for C^a_{ei} were determined by Lee et al. (1992) for samples in the EPRI survey (EPRI, 1993). The solid line corresponds to an ideal mixture. Dashed lines correspond to concentrations that deviate from the ideal by a factor of 2.

Table 1

Impact of manufactured gas process on tars produced in the U.S.

Product	Time Period	Process	Tar Properties & Composition
Coal gas (coke plants)	1800's–1918	Bituminous coal was heated in beehive ovens to create coke. Coal gas was not captured.	Negligible tar production.
	1892–1918	Facilities upgraded to byproduct coke ovens, allowing the capture of o -gases and operating from 850–900°C.	Primarily unsubstituted aromatic compounds. Contain tar acids, tar bases. Water content 3–7%.
Coal gas (gas plants)	Before 1850	Bituminous coal was heated in cast iron horizontal retorts from 600–800°C.	Similar to coal tar from carbonization. Lower temperatures resulted in more heterocyclics and tar acids.
	After 1850	Facilities switched to clay retorts allowing temperatures >900°C.	Higher temperatures resulted in more aromatics and less acids.
	After 1910	Facilities switched to vertical retorts. Operating temperatures lower than horizontal retorts.	More heterocylics. Tar acids 5–10%.
Carburetted water gas	Before 1910	Coke or anthracite coal was heated in the presence of steam. Oil was sprayed into emissions to crack the oil. Oil was predominantly paraffinic.	Primarily aromatics. Absent of tar acids and bases. Water content 50–90% but easily separated.
	After 1910	Most facilities switched to heavier, asphaltic oils mostly from Texas.	Higher density. 68% of these facilites reported problems separating emulsions.
	1910–1930	Many facilities switched to bituminous coal.	Higher density. 100% of these facilites reported problems separating emulsions. Composition more closely resembled coal tar.
	After 1940	Many facilities forced to use heavy fuel oil fractions.	Higher density and continued difficulty separating emulsions.
Oil gas	Before 1919	Oils were heated to crack hydrocarbons into smaller molecules. Mostly used in the West. Used raw crude.	Primarily aromatics. Almost no tar acids and bases. Some problems with emulsions.
	After 1919	Facilities forced to use heavier residual oil.	Increased emulsions. More difficult to break.

Sources: Adam (1932), Harkins et al. (1988), Hatheway (2002), Murphy et al. (2005), and Hamper (2006).

Table 2

Historic percent composition data for manufactured gas tars

Fraction	Component	Coal tar[a]	Water-gas tar
Light oil (170–270°C)	Crude benzene and toluene	0.3	1.2[b]
	Coumarone, indene, etc.	0.6	2.6[c]
	Xylenes, cumenes, and isomers	1.1	1.2[b]
	Total light oil	2.0	
Middle and heavy oils (170–270° C)	Naphthalene	10.9	8.0[b]
	Unidentified oils in range of naphthalene and methylnaphthalenes	1.7	
	α-Monomethylnaphthalene	1.0	
	β-Monomethylnaphthalene	1.5	
	Dimethylnaphthalenes	3.4	
	Acenaphthene	1.4	
	Unidentified oil in range of acenaphthene	1.0	
	Fluorene	1.6	
	Unidentified oil in range of fluorene	1.2	
	Total middle and heavy oils	23.7	
Anthracene oil (270–350°C)	Phenanthrene	4.0	
	Anthracene	1.1	0.29[b]
	Carbozole and kindred nonbasic nitrogen-containing bodies	2.3	
	Unidentified oils in anthracene range	5.4	
	Total anthracene oil	12.8	
Other	Phenol	0.7	
	Phenol homologs (largely cresols and xylenols)	1.5	
	Tar bases (mostly pyridine, picolines, lutidines, quinolines, and acridine)	2.3	
	Yellow solids and pitch oils	0.6	
	Pitch greases	6.4	
	Resinous bodies	5.3	
	Pitch (238°C melting point)	44.7	

Temperature ranges from Porter (1924); pg 323.

[a] Weiss and Downs (1923);

[b] Downs and Dean (1914)

[c] Brown and Howard (1923)

Table 3

Typical analyses of U.S. tars in the early to mid 1900s

Analyses	Coal tars			Water-gas tars		Oil-gas tar
	HR	CO	VR	LG	HG	FG
Naphthalene, % by vol.[a]	5.31	7.45	0.55	-	7.8	11.4
Tar acids, % by vol.[b]	2.6	3.6	10.5	0.0	0.0	0.5
Sulfonation residue, % by vol.[b]	0.5	0.1	2.1	3.3	2.1	0.5
Distillation, % by wt.[b]						
up to 170°C	0.0	0.3	1.8	2.0	0.2	0.8
up to 235°C	6.0	9.9	14.8	17.7	11.6	4.0
up to 270°C	13.8	17.4	25.2	34.2	29.0	12.7
up to 300°C	20.0	25.0	32.0	45.0	37.8	21.6
up to 335°C	23.1	32.1	40.3	62.8	48.8	29.0
up to 355°C	27.4	38.0	50.0	69.3	57.3	35.8
Residue	72.6	62.0	50.0	30.7	42.7	64.2

HR=horizontal retort; *CO*=coke oven; *VR*=vertical retort; *LG*=light gas oil; *HG*=heavy gas oil *FG*=fuel gas oil

[a]Rhodes (1945) for coal tars, Rhodes (1966b) for water-gas and oil-gas tars;

[b]Phelan and Rhodes (1966)

Table 4

Composition of unweathered and weathered tar DNAPLs

Type	Constituent	Fresh tars		FMGP tars						
				Well samples					Holding tanks	
				Site 1[e]	Site 4[e]	Site 5[e]	Str., PA[c]	Balt, MD[d]	Site 7[e]	Site 9[e]
		Coal[a]	Coal[b]	Water	Water	Coal	Water	Water	Coal	Coal
Total as % wt.	Quantified MAH's	–	1.5	0.97	0.38	2.5	1.2	0.73	0.37	0.36
	PP MAH's	–	0.10	0.45	0.036	1.5	0.1	0.4	0.12	0.17
	Quantified PAH's	54	37	25	18	33	46	28	2.5	6.2
	PP PAH's	46	37	24	18	32	17	23	2.4	6.0
PP MAH mg/kg	Benzene	–	950	550	4	4 970	500	1 000	790	450
	Toluene	–	1 074	2 120	53	7 000	940	–	1 310	1 060
	Ethylbenzene	–	44	1 860	300	2 700	–	3 400	400	170
PP PAH mg/kg	Naphthalene	148 000	140 900	70 000	52 000	135 000	21 600	100 000	6 540	21 400
	2-Methylnaphthalene	13 700	16 100	33 400	37 400	34 100	37 500	53 000	2 080	5 770
	1-Methylnaphthalene	6 310	6 900	23 500	21 500	19 600	38 000	–	1 170	3 320
	Acenaphthylene	37 800	19 900	610	12 100	17 800	6 800	3 700	1 180	530
	Acenaphthene	1 100	3 100	11 900	900	1 650	15 200	13 000	270	500
	Fluorene	20 800	16 900	11 600	6 870	1 150	14 000	1 800	1 080	2 100
	Phenanthrene	65 300	55 100	32 600	17 000	34 600	21 200	1 600	3 130	7 000
	Anthracene	15 400	13 500	8 570	5 420	7 670	5 900	20 000	980	1 080
	Fluoranthene	47 000	29 500	13 400	4 760	12 600	3 000	5 500	1 900	4 150
	Pyrene	34 500	21 300	13 200	6 890	17 900	5 000	3 200	1 000	3 080
	Benzo[a]anthracene	14 100	10 800	4 900	2 340	5 130	3 100	10 000	610	1 470
	Chrysene	9 520	7 600	5 100	2 340	6 470	2 700	3 600	620	1 880
	Benzo[b]fluoranthene	9 500	11 700	2 150	1 350	3 130	–	4 000	490	1 150
	Benzo[k]fluoranthene	5 920	–	2 950	610	2 850	–	1 600	360	850
	Benzo[a]pyrene	13 400	7 400	3 900	1 560	6 420	–	3 600	500	1 330
	Indeno[123-cd]pyrene	7 980	4 000	2 610	1 080	4 890	–	–	790	1 720
	Dibenzo[ah]anthracene	996	700	490	140	640	–	400	180	350
	Benzo[ghi]perylene	7 260	2 700	3 110	1 270	7 090	–	–	960	2 290

Type	Constituent	Fresh tars		FMGP tars						
				Well samples					Holding tanks	
				Site 1[e]	Site 4[e]	Site 5[e]	Str., PA[c]	Balt, MD[d]	Site 7[e]	Site 9[e]
		Coal[a]	Coal[b]	Water	Water	Coal	Water	Water	Coal	Coal
Heterocyclic mg/kg	Quinoline	–	–	2.7	0.9	5.2	–	–	3.3	560
	Acridine	–	–	1 000	25	14	–	–	42	33
	Carbazole	–	–	50	200	160	–	–	140	620
	Dibenzothiophene	–	–	–	2 020	3 230	–	–	1 600	ND
Inorganic mg/kg	Arsenic	–	–	20	9.3	23	–	–	3.0	3.6
	Chromium	–	–	1.1	<1	1.8	–	–	36	2.4
	Lead	–	–	1.0	6.5	1.4	–	–	8.1	37
	Cyanide, Method 4500	–	–	<1	<1	2.3	–	–	5.4	360
Misc.	% Ash	–	–	0.02	0.01	0.2	Low	–	20	4.0
	% Moisture	–	–	0.03	0.10	1.7	Low	–	15	28

PP=priority pollutant plus two branched naphthalenes. Coal = coal tar; Water=water-gas tar;

[a] NIST (2006);

[b] Eberhardt and Grathwohl (2002);

[c] EPRI (1993);

[d] Peters and Luthy (1993);

[e] Ghoshal et al. (1996)

Table 5

Composition of solid tars recovered from at or near the ground surface at FMGP's

Type	Constituent	Site 2[c]	Site 3[c]	Site 6[c]
		Coal	Coal	Coal
Total as % wt.	Quantified MAH's	0.35	0.028	<0.01
	PP MAH's	0.20	0.006	<0.01
	Quantified PAH's	4.8	2.4	5.2
	PP PAH's	4.6	2.3	5.3
PP MAH mg/kg	Benzene	460	14	11
	Toluene	1 050	9	<1
	Ethylbenzene	450	37	<1
PP PAH mg/kg	Naphthalene	13 300	4 030	970
	2-Methylnaphthalene	7 450	3 080	700
	1-Methylnaphthalene	4 900	2 350	640
	Acenaphthylene	260	300	890
	Acenaphthene	340	1 150	460
	Fluorene	1 350	1 110	1 420
	Phenanthrene	5 210	3 470	11 300
	Anthracene	390	690	2 980
	Fluoranthene	1 500	1 360	8 520
	Pyrene	2 410	2 070	6 170
	Benzo[a]anthracene	750	450	1 920
	Chrysene	1 050	750	2 360
	Benzo[b]fluoranthene	1 240	270	1 540
	Benzo[k]fluoranthene	1 050	130	830
	Benzo[a]pyrene	1 820	390	4 110
	Indeno[123-cd]pyrene	1 400	690	3 500
	Dibenzo[ah]anthracene	ND	250	450
	Benzo[ghi]perylene	1 640	940	4 150
Heterocyclic mg/kg	Quinoline	3.5	0.9	30
	Acridine	4.7	1	71
	Carbazole	49	20	580
	Dibenzothiophene	620	580	ND
Inorganic	Arsenic	6.4	7.8	4.7
	Chromium	11	28	36
	Lead	50	44	930
	Cyanide, Method 4500	2.6	5.7	69
Misc.	% Ash	9.6	54	49
	% Moisture	5.6	7.4	5.2

PP=priority pollutant plus two branched naphthalenes. Coal = coal tar; ND = note detected [c] EPRI (1993)

Table 6

SARA analysis for crude oils compared to FMGP tars

Fraction	Percent composition								
	Crude oils[a]			FMGP tars					
				Well samples		Holding tanks			
	light	med.	heavy	Str. PA[b]	Balt. MD[c]	PA[d]	NY[d]	US[e]	US[e]
Saturates	53	37	31	8	–	–	–	0.1	0.0
Aromatics	37	44	36	41	98.4	–	–	22.6	27.0
Resins	9	16	22	15	0.4	–	–	3.3	7.2
Asphaltenes	0.8	3	7	34	1.1	20.9	36.4	–	–

[a] Mean values calculated from Hemmingsen et al. (2005);

[b] Peters and Luthy (1993)

[c] Barranco and Dawson (1999);

[d] Zheng and Powers (2003);

[e] Haeseler et al. (1999)

Table 7

Historic specific gravity and viscosity data for manufactured gas tars

Tar	Type	Specific gravity	Kinematic viscosity	Engler viscosity	Float test seconds		Softening point	Dynamic viscosity
		15.5/15.5°C	35°C cSt	40°C	50°C	32°C	°C	35°C cP
Coal	VR[a]	1.103	237					$2.6 \cdot 10^2$
	CO[a]	1.180	316					$3.7 \cdot 10^2$
	CO[b]	1.196		163	26[e]			$2.0 \cdot 10^3$
	CO[b]	1.198				38		$1.4 \cdot 10^3$
	CO[a]	1.226	2 850					$3.5 \cdot 10^3$
	HR[b]	1.240			24			$1.6 \cdot 10^3$
	HR[a]	1.249	14 090					$1.8 \cdot 10^4$
Water-gas	L[b]	1.061		1.7				$9.1 \cdot 10^0$
	L[b]	1.089		2.0				$1.5 \cdot 10^1$
	L[b]	1.125		11.8				$1.8 \cdot 10^2$
	H[b]	1.212				74		$5.0 \cdot 10^3$
	FO[b,d]	1.227				123		$2.1 \cdot 10^4$
Oil-gas	MT[c]	1.206		13.2				$4.6 \cdot 10^2$
	FO[b,d]	1.256				100		$1.2 \cdot 10^4$
	HT[c]	1.297				247		$7.6 \cdot 10^4$
	FO[c]	1.317					32.6	$5.0 \cdot 10^5$
	HT[c]	1.334					33.8	$6.6 \cdot 10^5$

Data were converted using a linear interpolation of data in Phelan and Rhodes (1966) Table 15–13. VR=vertical retort; CO=coke oven; HR=horizontal retort; L=light; H=heavy; FO=fuel oil MT=medium temperature; HT=high temperature

[a] Rhodes (1945);

[b] Rhodes (1966b);

[c] Pacific Coast Gas Association (1926) cited in Harkins et al. (1988)

[d] Density converted from 25/25°C to 15/15°C based on Weiss (1915);

[e] Used to estimate dynamic viscosity

Table 8

Bulk properties of FMGP tars

Sample	Location	Form	$\overline{Mw}$ (g/mol)	Specific Gravity[f]	Dynamic viscosity[f] (cP)
Fresh Coal Tar[a]		liquid	248	1.198 (−)	-
Well samples	Str. Pa[b]	liquid	210	1.005 (30)	10 (30)
	Balt. MD[c]	liquid	226	1.047 (25)	10 (37)
	Site 1[e]	liquid	250	1.083 (24)	67 (40)
	Site 4[e]	liquid	230	1.064 (24)	34 (40)
	Site 5[e]	liquid	250	1.133 (24)	140 (40)
Holding tanks	PA[d]	liquid	-	1.051 (25)	19 (25)
	Site 7[e]	viscous liquid	780	1.251 (24)	-
	Site 9[e]	viscous liquid	480	1.107 (24)	6 600 (40)
Surface samples	Site 2[e]	pliable solid	700	1.366 (24)	-
	Site 3[e]	pliable solid	440	1.423 (24)	-
	Site 6[e]	solid	1 600	1.424 (24)	-

[a] Eberhardt and Grathwohl (2002);

[b] Peters and Luthy (1993);

[c] Barranco and Dawson (1999)

[d] Hugaboom and Powers (2002);

[e] EPRI (1993);

[f] Temperature °C in parentheses

Table 9

Interfacial tension of tar samples as a function of pH

Sample	pH	γ^{nw} (dynes/cm)
Stroudsburg, PA[a]	NP	22
Baltimore, MD[b]	<9.1	23.5
	12.4	0.6
Pennsylvania[c]	7	~20
New York[c]	7	~25

NP=not provided; *nw*= NAPL and water interface;

[a]Villaume (1984);

[b]Barranco and Dawson (1999);

[c]Zheng and Powers (2003)

Table 10

Experimental Assessments of Tar DNAPL Remediation Approaches

Source	Methods	Result
Roy et al. 1995	Several 1-D columns packed with sand. Contaminated with Stroudsburg FMGP tar from 4–25% res. sat. Flushed with 80% n-butylamine.	Large amount of tar removed in the first 2 PV. Tar removal reduced to approx. constant value after ~10 PV. Tar still leaching after 40 PV.
Hugaboom and Powers 2002	Three 1-D columns packed with sand. Contaminated with Pennsylvania FMGP tar at ~87% res. sat. Flushed with water at varying pH to control wettability.	Reduced res. sat. after flushing under oil-wet conditions (pH=4.7) to 47%, water-wet conditions (pH=7.2 or 9.9) to ~30%.
Giese and Powers 2002	Several 1-D columns packed with sand. Contaminated with either of two synthetic NAPLs having varying viscosity (10 or 20 cP) at 75% res. sat. Wettability was altered using varying concentrations of dode-cylamine. Flushed with either water or polymer solutions.	Results similar for both NAPLs. Res. sat. reduced in water-wet systems to ~20% regardless of flushing solution. In oil-wet systems, reduced to ~45% using water flushing, ~35% using polymer solutions with $\kappa \cong 1$, ~20% using polymer solutions with κ=0.1.
Dong et al. 2004	2-D tank was packed with sand contaminated using tar from a FMGP in the United Kingdom. Tank was flushed with increasing concentrations of a poloxamine block copolymeric surfactant.	Tanks were assessed visually. Flushing with a 1% polymer solution mobilized the coal tar downward.

PV=pore volumes. κ=tar viscosity/polymer viscosity.